

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 : C08G 18/28, 18/67, D06M 15/576		A1	(11) International Publication Number: WO 92/19663 (43) International Publication Date: 12 November 1992 (12.11.92)		
(21) International Application Number: PCT/US92/03300		(81) Designated States: AT (European patent), AU, BE (European patent), CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, KR, LU (European patent), MC (European patent), NL (European patent), SE (European patent).			
(22) International Filing Date: 21 April 1992 (21.04.92)					
(30) Priority data: P 41 13 634.9 26 April 1991 (26.04.91) DE					
(71) Applicant: MINNESOTA MINING AND MANUFACTURING COMPANY [US/US]; 3M Center, Post Office Box 33427, Saint Paul, MN 55133-3427 (US).		Published <i>With international search report.</i>			
(72) Inventors: ALLEWAERT, Kathy ; COPPENS, Dirk ; FI-EUWS, Franceska ; Post Office Box 33427, Saint Paul, MN 55133-3427 (US).					
(74) Agents: TRUESDALE, Carole et al.; Post Office Box 33427, Saint Paul, MN 55133-3427 (US).					
(54) Title: FLUOROACRYLATE MONOMERS AND POLYMERS, PROCESSES FOR PREPARING THE SAME AND THEIR USE					
(57) Abstract					
The invention provides polymers or copolymers which are prepared by the polymerization of the reaction product of a diisocyanate with a perfluoro compound or an epichlorhydrinadduct thereof and (meth)acrylic esters of a three hydroxyl groups containing compound. Furthermore, the invention relates to fluoroacrylic monomers, a process for preparing the polymers or copolymers and a treatment agent comprising the polymers or copolymers of the invention and an environmentally acceptable solvent. Polymers and copolymers of the invention can be used for making textiles, papers, non-woven articles, leather, plastic, wood, metal, stone and cement water and oil repellent.					

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	FI	Finland	ML	Mali
AU	Australia	FR	France	MN	Mongolia
BB	Barbados	GA	Gabon	MR	Mauritania
BE	Belgium	GB	United Kingdom	MW	Malawi
BF	Burkina Faso	GN	Guinea	NL	Netherlands
BG	Bulgaria	GR	Greece	NO	Norway
BJ	Benin	HU	Hungary	PL	Poland
BR	Brazil	IE	Ireland	RO	Romania
CA	Canada	IT	Italy	RU	Russian Federation
CF	Central African Republic	JP	Japan	SD	Sudan
CG	Congo	KP	Democratic People's Republic of Korea	SE	Sweden
CH	Switzerland	KR	Republic of Korea	SN	Senegal
CI	Côte d'Ivoire	LI	Liechtenstein	SU	Soviet Union
CM	Cameroon	LK	Sri Lanka	TD	Chad
CS	Czechoslovakia	LU	Luxembourg	TG	Togo
DE	Germany	MC	Monaco	US	United States of America
DK	Denmark	MG	Madagascar		

- 1 -

**FLUOROACRYLATE MONOMERS AND POLYMERS,
PROCESSES FOR PREPARING THE SAME AND THEIR USE**

- The present invention relates to polymers or
5 copolymers obtainable by the polymerization of the
reaction products of diisocyanates with a perfluoro
compound or an epichlorhydrin adduct thereof and
methacrylic esters of a compound containing three
hydroxyl groups. Furthermore, the invention relates to
10 a fluoroacrylic monomer as an intermediate product and
to a process for preparing the polymers or copolymers
and its use providing water and oil repellency to
textiles, papers, non-woven articles, leather, plastic,
wood, metal, glass, stone and cement.
- 15 Furthermore, the invention relates to a
treatment agent which comprises the polymers or
copolymers according to the invention and an
environmentally acceptable solvent.

During the past years there is a growing
20 market demand for fluorochemical products with good oil
and water repellency for the treatment of various
substrates. The use of fluoroacrylic polymers for
products with good oil and water repellency for
treatment of substrates is described in U.S. Pat. No.
25 4,778,915. This reference describes fluoroacrylic
monomers and polymers which are prepared from a
diisocyanate, a polyfluoro compound and an acrylic or
methacrylic ester of a 2-alkylaminoethanol, preferably
2-t-butylaminoethyl-methacrylate. These fluoroacrylic
30 polymers can be used for the treatment of textiles or
leather.

German Patent Publication No. A-31 19 058
describes a treatment agent for textile filaments
consisting of a aqueous dispersion of a perfluoroalkyl
35 ester of a citric acid urethane and a fluorinated
alcohol and the reaction product of an epoxy resin, a

- 2 -

polymer with a carboxyl function and a aqueous solution of a tertiary amine.

U.S. Pat. No. 4,612,356 describes homo- and co-addition polymers of di-perfluoroalkyl carbamyl 5 group- containing (meth)acrylate monomers and their use as oil and water repellency treatment of textiles.

European Patent Publication No. 0 100 277 describes a coating for infrared transparency films consisting of a copolymer formed from one fluorocarbon 10 monomer prepared from equimolar amounts of N-ethylperfluoroctyl-sulfonamidoethanol, 2,4-toluene di-isocyanate and hydroxypropylmethacrylate.

U.S. Pat. No. 4,920,190 discloses fluorinated acrylic monomers prepared by reacting in a first stage 15 toluene 2,4-diisocyanate with an equimolar amount of a polyfluorinated compound to form a fluorinated urethane-isocyanate and then reacting this urethane-isocyanate with an equimolar amount of an acrylic ester.

20 The polymers and copolymers which are used for the preparation of treatment agents for making substrates oil and water repellent have the disadvantage that they are only soluble in environmentally unacceptable solvents such as 1,1,1-trichloroethane and 25 trichlorotrifluoroethane in which they show a good performance. During the past years, there is a growing market demand for fluorochemical products which are soluble in environmentally acceptable solvents such as isopropanol. U.S. Pat. No. 4,778,915 describes a 30 fluoroacrylic polymer which is soluble in isopropanol and from which aqueous dispersions can be prepared. The disadvantage of the treatment agents described in this reference is that the substances only show a very low performance in comparison to the treatment agents which 35 are dissolved in environmentally unacceptable solvents.

The present invention provides polymers or copolymers comprising the polymerization product of (a)

- 3 -

- diisocyanate with a perfluoro compound or an epichlorhydrin adduct thereof, said perfluoro compound having a terminal hydroxyl, thiol, primary or secondary amino group attached to the perfluoroalkyl group
- 5 directly via an alkylene bridge or indirectly via an alkylene bridge and a sulphonamido, carbonamide, ether, thioether, sulphonyl or carboxylic ester group between the perfluoroalkyl and the alkylene group, and (b) (meth)acrylic esters of a three hydroxyl groups
- 10 containing compound.

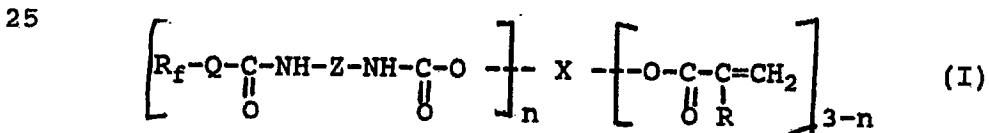
The fluoroacrylate polymers of the present invention can be used as treatment agents for making substrates oil and water repellent and are easily soluble in environmental acceptable solvents like

15 isopropanol and water and provide good oil and water repellency.

In a preferred embodiment the (meth)acrylic esters are the reaction products of an equimolar reaction between (meth)acrylic acid and a three

20 hydroxyl group containing compound.

The reaction product which is used for the preparation of the polymers or copolymers according to the invention can be represented by the following general formula:



The fluoroaliphatic group is designated herein as R_f . R_f is a stable, inert, nonpolar, preferably saturated monovalent moiety which is both oleophobic and hydrophobic. A fluorinated oligomer preferably comprises from 2 to about 25 R_f groups and preferably comprises about 5 percent to about 30 percent, and more preferably about 8 percent to about 20 percent fluorine by weight based on the total weight of the oligomer, the loci of the fluorine being

- 4 -

essentially in the R_f groups. R_f preferably contains at least about 3 carbon atoms, more preferably 3 to about 20 carbon atoms, and most preferably about 6 to about 12 carbon atoms. R_f can contain straight chain,
5 branched chain, or cyclic alkyl groups. R_f is preferably free of polymerizable olefinic unsaturation and can optionally contain catenary heteroatoms such as oxygen, divalent or hexavalent sulfur, or nitrogen. It is preferred that each R_f contain about 40% to about
10 78% fluorine by weight, more preferably about 50% to about 78% fluorine by weight. The terminal portion of the R_f group contains a fully fluorinated terminal group. This terminal group preferably contains at least 7 fluorine atoms, e.g., CF₃CF₂CF₂, (CF₃)₂CF, CF₂SF₅, or
15 the like. Perfluorinated aliphatic groups, i.e., those of the formula C_nF_{2n+1}, are the most preferred embodiments of R_f.

Linking group Q can be a covalent bond, a heteroatom, such as O or S, or an organic moiety. The
20 linking group Q is preferably an organic moiety containing 1 to about 20 carbon atoms, and optionally containing oxygen, nitrogen-, or sulfur-containing groups or a combination thereof, and preferably free of active hydrogen atoms. Examples of structures suitable
25 for linking group Q include straight chain, branched chain, or cyclic alkylene, arylene, aralkylene, oxy, oxo, thio, sulfonyl, sulfinyl, imino, sulfonamido, carbonamido, carbonyloxy, urethylene, ureylene, and combinations thereof such as sulfonamidoalkylene.
30 Preferred linking groups Q can be selected according to ease of preparation and commercial availability. Below is a partially representative list of suitable organic Q groups. For the purposes of this list, each k is independently an integer from 1 to about 20, g is an
35 integer from 0 to about 10, h is an integer from 1 to about 20, R' is hydrogen, phenyl, or alkyl of 1 to

- 5 -

about 4 carbon atoms, and R'' is alkyl of 1 to about 20 carbon atoms.

- SO₂NR'(CH₂)_kO(O)C-
- CONR'(CH₂)_kO(O)C-
- 5 -(CH₂)_kO(O)C-
- CH₂CH(OH)CH₂O(O)C-
- CH₂CH(OR'')CH₂O(O)C-
- 10 -(CH₂)_kC(O)O-
- (CH₂)_kSC(O)-
- (CH₂)_kO(CH₂)_kO(O)C-
- (CH₂)_kS(CH₂)_kO(O)C-
- 15 -(CH₂)_k(OCH₂CH₂)_kO(O)C-
- CH₂)_kSO₂(CH₂)_kO(O)C-
- SO₂NR(CH₂)_kO(CH₂CH₂)_kO(O)C-
- 20 -(CH₂)_kSO₂NR(CH₂)_kO(O)C-
- (CH₂)_kSO₂-
- SO₂NR'(CH₂)_k-
- OC₆H₄CH₂O(O)C-
- 25 -SO₂NR(CH₂)_hO(CH₂CH(O)CH₂Cl)_gCH₂CH(O)C(O)CH₂Cl
- (CH₂)_hO(CH₂CH(O)CH₂Cl)_gCH₂CH(O)C(O)CH₂Cl
- (CH₂)_hO(CH₂CH₂O)gCH₂CH₂OOC(O)
- 30 -(CH₂)_hO(CHCH₂O)gCHCH₂OOC(O)CH₃
- (CH₂)_hO((O)C(CH₂)₆O)gC(O)(CH₂)₆OC(O)
- (CH₂)_hO((O)C(CH₂)₆NH)gC(O)(CH₂)₆NHC(O)
- C(O)O(CH₂)₂OC(O)NH(CH₂)₂OC(O)

30 For linking R_f, Q is preferably alkylene or sulfonamido, or sulfonamidoalkylene.

R is a hydrogen or a methyl group, Z is a divalent aliphatic, alicyclic or aromatic connecting group.

35 The divalent organic linking group Z connects successive isocyanate moieties. Illustrative linking groups Z are alkylene groups, such as ethylene,

- 6 -

isobutylene, hexylene, and methylenedicyclohexylene, having 2 to about 20 carbon atoms, aralkylene groups, such as $-\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2-$ and $-\text{C}_6\text{H}_4\text{CH}_2\text{C}_6\text{H}_4-$, having up to 20 carbon atoms, arylene groups, such as tolylene,

5 - $C_6H_3(CH_3)-$, poly(oxyalkylene) groups, such as
-(C_2H_4O)_y C_2H_4- where y is 1 to about 5, and various
combinations of these groups. Such groups can also
include other hetero moieties (besides -O-), including
-S- and -N-. However, Z is preferably free of groups
0 with active hydrogen atoms.

X is a trivalent connecting group. X can be aliphatic, aromatic or cycloaliphatic. X is preferably an aliphatic group containing at least 3 carbon atoms and which may be straight chain or branched.

15 Particularly preferred are residues of alkanetriols and nitriloalkanols. Examples of such groups include, for example, the residues of trimethanolethane, triethanolamine, 1,3,5-trihydroxybenzene and 1,3,5-tris(S-hydroxyethyl) cyanuric acid.

20 n is 1 or 2, preferably 2.

The fluorinated (meth)acrylic monomers of the formula (I) according to the invention may be prepared by reacting a diisocyanate of formula

$$25 \quad O = C = N - Z - N = C = O \quad (II)$$

wherein Z is defined as above with preferably equimolar quantities of a polyfluoro compound of the formula

$$30 \quad R_f = Q = H \quad (III)$$

wherein R_f and Q are defined as above and a (meth)acrylic ester of the formula

$$35 \quad (\text{HO})_n \left[\begin{array}{c} \text{X}-\text{O}-\underset{\substack{\text{O} \\ |} }{\text{C}}-\underset{\substack{| \\ \text{R}}} {\text{C}} = \text{CH}_2 \\ \end{array} \right]_{3-n} \quad (\text{IV})$$

- 7 -

wherein n is 1 or 2, preferably 2 and R and X are as defined as above.

Examples of diisocyanates which may be used include aromatic diisocyanates such as 2,4 and/or 2,6 toluene diisocyanate (TDI), 4,4'-diphenylmethane diisocyanate (MDI), and (MTMXDI)-metatetramethylxylene diisocyanate. Furthermore, aliphatic diisocyanates such as hexamethylene diisocyanate (HMDI), trimethyl-hexamethylenediisocyanate (TMHMDI), decamethylene diisocyanate and Dimer Diisocyanate (DDI 1410 from Henkel) and alicyclic diisocyanates such as 4,4'-methylene bis (cyclohexyl isocyanate), trans 1,4-cyclohexyldiisocyanate (CHDI), isophorondiisocyanate (IPDI) can be used. Among these diisocyanates, 2,4-toluene diisocyanate (TDI) is especially preferred by itself or mixed with the 2,6 isomer.

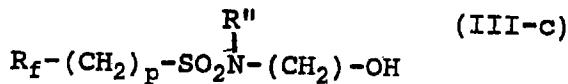
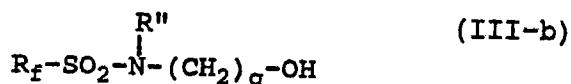
As the compound of formula (III), a perfluoro compound or an epichlorhydrin adduct thereof is used, the compound having a terminal hydroxyl, thiol, primary or secondary amino group attached to the perfluoroalkyl group directly via alkylene bridge or indirectly via an alkylene bridge and a sulphonamido, carbonamide, ether, thioether, sulphonyl or carboxylic ester group between the perfluoroalkyl and the alkylene group and (meth)acrylic esters of a three hydroxyl groups-containing compound.

Examples of such polyfluoro compounds include, but are not limited to, those of the following formulas:

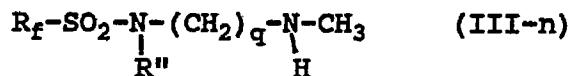
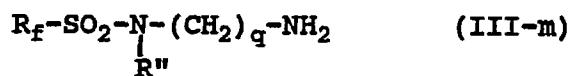
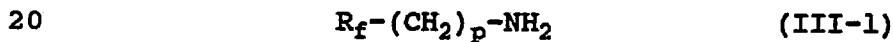
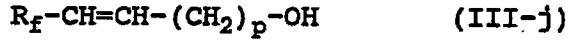
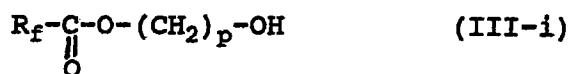
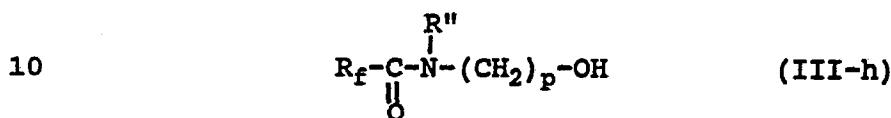
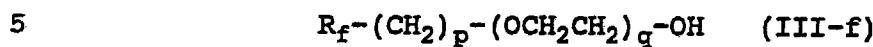
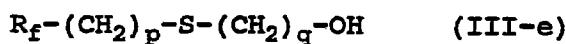
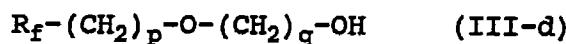
30



35



- 8 -



in which R_f has the same meaning as defined above and
 R'' is hydrogen or an alkyl group and the symbols p and
30 q which can be identical or different each denote an
integer ranging from 1 to 20 and preferably equal to 2
or 4. Among these compounds (III), those with a
hydroxyl functionality are preferred. Particularly
preferred are the N-
35 alkyl(perfluoroctane)sulphonamidoalkyl alcohols or
telomer alcohols listed in Table 1 as fluorochemical
alcohols.

- 9 -

As examples of esters of the formula (IV) which may be employed for the formation of the polymer according to the invention, acrylic and methacrylic esters of the three hydroxyl group containing compound 5 can be used. Preferred are alkanetriols or nitrilotri- alkanols. Particularly preferred are the three hydroxyl group containing compounds listed in Table 1 (b_1 - b_5). The products referring to formula (IV) can be prepared by known techniques. Thus, equimolar amounts of 10 alkanetriol can be reacted with acrylic or methacrylic acid or alternatively acryloylchloride or methacryloylchloride can be reacted with alkanetriol. Preferably, the (meth)acrylic ester mixture of the alkanetriol is prepared by reacting 0.8 to 1.5 mol acrylic acid per 15 mol of alkanetriol.

The synthesis of the fluorinated (meth)acrylate monomer (I) according to the invention is preferably conducted in an organic solvent such as ketone, ester, aromatic solvents, alkane, halogenated 20 hydrocarbons, dimethylformamide, N-methylpyrrolidone or acetonitrile. Especially preferred are methylethylketone, methylisobutylketone, ethylacetate, butylacetate, toluene, xylene, benzene, hexane, heptane, cyclohexane, tetrahydrofuran, diethylether, 25 diethylene glycol dimethylether, 1,1,1-trichloroethane, trichlorotrifluoroethane.

The addition reactions of the polyfluoro compound R_f-Q-H (III) and of the (meth)acrylic esters (IV) to the isocyanate groups are carried out between 30 30°C and 90°C under an inert atmosphere and in the absence of water. Since the reaction is very slow, it is preferred to conduct the reaction in the presence of a catalyst such as, for example, a tertiary amine, a tin salt and/or a lead salt. Preferably used are 35 triethylamine, triethylenediamine, N-methylmorpholine, dibutyltindilaurate, tin octanoate, lead naphthonate.

- 10 -

The amount of catalyst is usually from 0.05 to 1 % based on the total weight of the reactants.

In order to limit the formation of symmetrical diaddition products, in a preferred embodiment the perfluoro compound R_f-Q-H (III) is added to the isocyanate compound and reacted under inert atmosphere without a catalyst. The (meth)acrylic ester is added in a second step and reacts very readily with the remaining free isocyanate groups when using a combination of a tertiary amine and a tin like catalyst.

The invention further relates to the polymers containing repeating units of the formula (I) in which the various symbols have the same meanings as defined before. The polymers may be prepared from the monomers of formula (I) by homopolymerization or by copolymerization with other monomers.

Examples of hydrocarbon and fluorinated comonomers which may be used in the present invention include moieties derived from vinyl ethers, vinyl ester, ally esters, vinylketones, styrene, vinylamide, acrylamide, maleates, fumarates, acrylates and (meth)-acrylates. Preferably used are comonomers from acrylates and methacrylates. As examples of hydrocarbon comonomers which may be used within the scope of the present invention the following are included:

lower (halogenated or otherwise) olefinic hydrocarbons such as ethylene, propylene, isobutene, 3-chloro-1-isobutene, butadiene, isoprene, chloro- and dichlorobutadiene, fluoro- and difluorobutadienes, 2,5-dimethyl-1,5-hexadiene and diisobutylene;

vinyl, allyl or vinylidene halides such as vinyl or vinylidene chloride, vinyl or vinylidene fluoride, allyl bromide and methallyl chloride; styrene and its derivatives, such as vinyltoluene, α -methylstyrene, α -cyanomethylstyrene, divinyl benzene, and N-vinylcarbazole;

- 11 -

vinyl esters such as vinyl acetate, vinyl propionate, vinyl esters of acids known commercially under the name of "Versatic Acids", vinyl isobutyrate, vinyl senecioate, vinyl succinate, vinyl isodecanoate, vinyl stearate and divinyl carbonate;

allyl esters such as allyl acetate and allyl heptanoate;

alkyl vinyl ethers or alkyl allyl ethers (halogenated or otherwise), such as cetyl vinyl ether,
10 dodecyl vinyl ether, isobutyl vinyl ether, ethyl vinyl

ether, 2-chloroethyl vinyl ether and tetraallyl oxyethane;

vinyl alkyl ketones such as vinyl methyl
15 ketone; unsaturated acids such as acrylic, methacrylic, α -chloroacrylic, crotonic, maleic, fumaric, itaconic, citraconic and senecioic acids, their anhydrides and their esters such as vinyl, allyl methyl, butyl, isobutyl, hexyl, heptyl, 2-ethylhexyl, cyclohexyl,
20 lauryl, stearyl or alkoxy ethyl acrylates and methacrylates, dimethyl maleate, ethyl crotonate, methyl hydrogen maleate, butyl hydrogen itaconate, glycol or polyalkylene glycol diacrylates and dimethacrylates such as ethylene glycol dimethacrylate
25 or triethylene glycol dimethacrylate, dichlorophosphatoalkyl acrylates and methacrylates such as dichlorophosphatoethyl methacrylate, and bis(methacryloyloxyethyl) hydrogen phosphate and methacryloyloxypropyltrimethoxysilane;
30 acrylonitrile, methacrylonitrile, 2-chloroacrylonitrile, 2-cyanoethyl acrylate, methylene glutaronitrile, vinylidene cyanide, alkyl cyanoacrylates such as isopropyl cyanoacrylate, tris(acryloyl)hexahydro-s-triazine,
35 vinyltrichlorosilane, vinyltrimethoxysilane, vinyltriethoxysilane and N-vinyl-2-pyrrolidone;

- 12 -

allyl alcohol, allyl glycolate,
isobutenediol, allyloxyethanol, o-allylphenol,
divinylcarbinol, glycerol allyl ether, acrylamide,
methacrylamide, maleamide and maleimide, N-
5 (cyanoethyl)acrylamide, N-isopropyl acrylamide, di-
acetoneacrylamide, N-(hydroxymethyl) acrylamide and
methacrylamide, N-(alkoxymethyl)-acrylamides and
methacrylamides, glyoxal bisacrylamide, sodium acrylate
or methacrylate, vinylsulphonic and styrene-p-sulphonic
10 acids and their alkali metal salts, 3-amino-
crotononitrile, monoallylamine, vinyl-pyridines,
glycidyl acrylate or methacrylate, allyl glycidyl
ether, acrolein, N,N-dimethylaminoethyl methacrylate or
N-tert-butylamino ethyl methacrylate are used.

15

Fluorinated comonomers and methods for the preparation thereof are known and disclosed, for example, in U.S. Pat. No. 2,803,615 (Ahlbrecht et al.). Examples of such compounds include general classes of
20 fluorochemical olefins such as acrylates, methacrylates, vinyl ethers, and allyl compounds containing fluorinated sulfonamido groups, acrylates or methacrylates derived from fluorochemical telomer alcohols, fluorochemical thiols and the like.

25

Preferred compounds include, for example, N-methyl perfluoroctanesulfonamidoethyl acrylate, N-methyl perfluoroctanesulfonamidoethyl methacrylate, N-ethyl perfluoroctanesulfonamidoethyl acrylate, the reaction product of isocyanatoethyl methacrylate and N-
30 methylperfluoroctanesulfonamidoethyl alcohol, perfluoroctyl acrylate, N-methyl perfluoroctane-sulfonamidoethyl vinyl ether, and N-allyl perfluoroctanesulfonamide, and others such as perfluorocyclohexyl acrylate, and tetrameric
35 hexafluoropropyleneoxide dihydroacrylate.

The fluoro copolymers according to the invention may be prepared in a per se known manner by

- 13 -

polymerization in an organic solvent or in an aqueous emulsion. Since the water and oil repellent agent according to the invention is usually used in solution, the solution polymerization is preferred. The process 5 is usually carried out between 50°C and 110°C. The total monomer concentration may vary from 5 to 60% by weight. The polymerization in a solvent medium may be performed in the same solvents which are used for the synthesis of the fluoroochemical diurethaneacrylic 10 monomer (I).

The polymerization is carried out in the presence of initiators used in an amount of 0.1 to 1.5% based on the total weight of the monomers employed. It is possible to use peroxides such as benzoylperoxide, 15 lauroylperoxide, succinylperoxide, and tert-butyl perpivalate, or azo compounds such as for example, 2,2'-azobisisobutyronitrile, 4,4'-azobis (4-cyanopentanoic acid) and azodicarbonamide. If required, the length of the polymer chains may be regulated by 20 means of chain transfer agents such as alkylmercaptan, carbon tetrachloride or triphenylmethane, used in a proportion of 0.05 to 1% based on the total weight of the monomers.

The polymerization in aqueous emulsion may be 25 carried out according to well known methods. Various surfactants such as anionic, cationic, nonionic or amphoteric surfactants may be employed as the dispersant. These surfactants may be used alone or in combination.

To more easily emulsify the monomer it is generally advantageous to use organic solvents such as, for example, ketones, glycols or ethylene glycol ethers, alcohols or mixtures of this solvents. In general, the quantity of solvent should not exceed the 35 total weight of the monomer.

Water soluble products such as inorganic peroxides and persalts or water insoluble initiators

- 14 -

such as organic peroxides and the azo compounds referred to before may also be used as polymerization initiator in an aqueous emulsion.

The polymers or copolymers of the invention
5 can be used as treatment agents in a solution of an environmentally acceptable solvent. Preferred solvents are alkanoles, ketones, esters or mixtures thereof. Especially preferred is isopropanol.

Also polymer emulsions can be prepared by
10 diluting the polymer according to the invention with water.

The polymers or copolymers of the invention and the treatment agents can be used for providing water and oil repellency to textiles, papers, non-woven
15 articles, leather, plastics, wood, metals, glass, stone and cement. There is no particular restriction on the methods used to apply the polymers or copolymers of the invention to the substrates. The application of the diluted products may be carried out by spraying,
20 dipping or padding followed by drying at ambient temperature or a temperature which may range up to 150°C. The quantity of polymer to be employed may vary within wide limits, depending on the nature of the substrate and the fluorine content of the polymer.

25 In the following examples and comparative examples the water repellency (WR), the oil repellency (OR) and the spray rating (SR) were measured using the following tests.

30 Water Repellency Test

The aqueous stain or water repellency of treated sample is measured using a water/isopropyl alcohol test, and is expressed in terms of a water repellency rating of the treated fabric. Treated
35 fabrics which are penetrated by or resistant to a 100 percent water/ zero percent isopropyl alcohol mixture (the least penetrating of the test mixtures) are given

- 15 -

a rating of 100/0, whereas treated fabrics resistant to a zero percent water/100 percent isopropyl alcohol mixture (the most penetrating of the test mixtures) are given a rating of 0/100. Other intermediate values are determined by use of other water/isopropyl alcohol mixtures, in which the percentage amounts of water and isopropyl alcohol are each multiples of 10. Results are reported as an average of replicate testing. The water repellency rating corresponds to the most penetrating mixture which does not penetrate or wet the fabric after 30 seconds contact. In general, a water repellency rating of 90/10 or better, e.g., 80/20, is desirable for fabric.

15 Oil Repellency Test

The oil repellency of treated carpet and textile sample is measured by the American Association of Textile Chemists and Colorists (AATCC) Standard Test Method No. 118-1983, which test is based on the resistance of treated fabric to penetration by oils of varying surface tensions. Treated fabrics resistant only to "Nujol", a brand of mineral oil and the least penetrating of the test oils, are given a rating of 1, whereas treated fabrics resistant to heptane (the most penetrating of the test oils) are given a value of 8. Other intermediate values are determined by use of other pure oils or mixtures of oils, as shown in the following table:

- 16 -

Standard Test Liquids

	5	AATCC OIL Repellency Rating Number	Composition
10	1	"Nujol"	
	2	65:35 "Nujol": n-hexadecane by volume @ 70° F. (21° C.)	
	3	n-hexadecane	
	4	n-tetradecane	
	5	n-dodecane	
	6	n-decane	
	15	n-octane	
	8	n-heptane	

The rated oil repellency corresponds to the
20 most penetrating oil (or mixture of oils) which does
not penetrate or wet the fabric 30 seconds contact.
Higher numbers indicate better oil repellency. In
general, an oil repellency of 2 or greater is desirable
for fabric.

25

Spray Rating Test

The resistance of a treated substrates to
wetting with water was measured using a "Water
Repellency Spray Test as described in American
30 Association of Textile Chemists and Colorists Technical
Manual, 1977, 53, 245. Samples are rated on a scale of
0 to 100 with 0 indicating complete wetting of the
upper and lower surfaces of the substrate and with a
100 indicating no wetting.

35

Examples

The following non-limiting examples show
embodiments of the invention. The reactants used in the
examples are listed in table 1.

40

- 17 -

TABLE 1

Code	Reactant Formulas	
<u>Polymerizable monomer</u>		
A ₁	CH ₂ =CH-COOH	Acrylic Acid
5 A ₂	CH ₂ =C(CH ₃)-COOH	Methacrylic Acid
<u>Polyols</u>		
B ₁	CH ₃ C(CH ₂ OH) ₃	
B ₂	CH ₃ CH ₂ C(CH ₂ OH) ₃	
10 B ₃	N(CH ₂ CH ₂ OH) ₃	
B ₄	HOCH ₂ CH(OH)CH ₂ OH	
B ₅	HOCH ₂ CH(OH)CH ₂ (CH ₂) ₃ OH	
<u>Isocyanates</u>		
15 TDI		
20	2,4 toluenediisocyanate	
MDI		4,4'-diphenylmethane diisocyanate
25 Desmodur W		4,4' methylene bis (cyclohexyl isocyanate)
DDI 1410	Dimer Diisocyanate MW = 600 (Henkel)	
30	<u>Fluorochemical alcohols</u>	
C ₁	C ₈ F ₁₇ SO ₂ N(Et)CH ₂ CH ₂ OH	
C ₂	C ₈ F ₁₇ SO ₂ N(Me)CH ₂ CH ₂ OCH ₂ CH(CH ₂ Cl)OH	
C ₃	C ₈ F ₁₇ SO ₂ N(Bu)CH ₂ CH ₂ OH	
35 C ₄	C ₈ F ₁₇ SO ₂ N(Me)(CH ₂) ₁₁ OH	
C ₅	C ₈ F ₁₇ SO ₂ N(Me)CH ₂ CH ₂ OH	
C ₆	C _n F _{2n+1} CH ₂ CH ₂ O	(n is about 8)
C ₇	C _n F _{2n+1} CH ₂ CH ₂ O(CH ₂ CHO) _n H CH ₂ Cl	

- 18 -

Preparation of the intermediate (Example 1)

To a 2 liter 3-necked flask equipped with a heating mantle, stirrer, thermometer, dean-stark and refluxcooler were charged the following:

5

	1,2,6-trihydroxyhexane	268.3 g
	Methacrylic Acid	172.18 g
	AMBERLYST 15 dry	13.2 g
	Heptane	189 g
10	MEHQ	0.66 g
	phenothiazine	0.66 g

10

The mixture was heated to reflux temperature and stirred for about 5 hours. Analysis by gas chromatography showed that the reaction had ended. A mixture containing mainly the monomethacrylate component and smaller amounts dimethacrylate and unreacted triol was obtained. Thereafter, the heptane was evaporated off and a viscous clear product was obtained. After dilution to 50% solids in isobutylmethylketone, the AMBERLYST beads were filtrated off. The product was stored until needed for further reaction.

20

Example 2

25 91.5 g dry isobutylmethylketone and 26.6 g (0.1 mol) Desmodur W (Bayer, 4,4'-methylene bis(cyclohexylisocyanate)), 64.9 g (0.1 mol) N-methyl (perfluorooctane) sulphonamidoethyl epi(I)alcohol ($C_8F_{17}SO_2N(Me)C_2H_4OCH_2CH(CH_2Cl)OH$), and 3 drops of 30 dibutyltindilaurate were charged into a 500 mL 3-necked flask equipped with a heating mantle, stirrer, thermometer, a reflux condenser and nitrogen inlet. Air was purged from the reaction flask with a stream of dry nitrogen, and then the temperature of the reaction 35 mixture was raised to 80°C and stirred for about 1 hour (analysis by infrared absorption indicated that the reaction had ended). Thereafter, the reaction mixture

- 19 -

- was cooled to about 50°C and 20.2 g (0.05 mol, 50% solids content) of the methacrylate solution prepared in Ex. 1, was added. The reaction mixture was again raised to 80°C for about 5 hours and was then cooled.
- 5 Infrared absorption analysis of a small portion of reaction mixture indicated that all of the isocyanate groups had been converted to urethane groups. 203.5 g of a yellow solution of a monomer according to the invention was obtained in this manner. This solution 10 contained 50% solids.

Examples 3 - 9

Following the general procedures of Examples 1 and 2, and using reactants shown in Tables 1 and 2, 15 additional fluoroochemical (meth)acrylate monomers according to the invention were prepared.

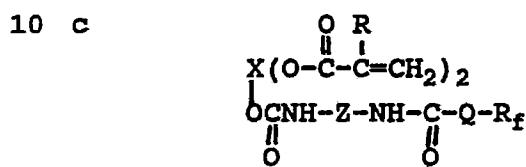
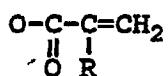
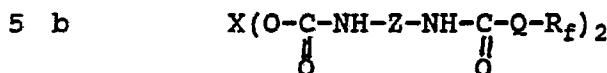
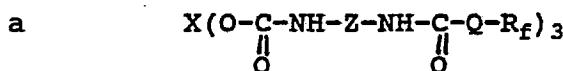
TABLE 2

Ex. 20 No.	Fluorochem. monomer	Isocyanate	Polyol	Polym.
2	C ₂	Desmodur W	B ₅	A ₂
25 3	C ₁	TDI	B ₂	A ₁
4	C ₃	MDI	B ₁	A ₂
5	C ₆	TDI	B ₂	A ₁
6	C ₁	MDI	B ₄	A ₂
7	C ₇	TDI	B ₂	A ₂
30 8	C ₅	DDI	B ₃	A ₂
9	C ₄	TDI	B ₂	A ₁

The general mixtures corresponding to the acrylate monomer mixtures are shown in Table 2A.

- 20 -

TABLE 2A



15 Example 10

Into a dry 500 ml three necked flask fitted with stirrer, addition funnel, a condenser, a thermometer, and nitrogen inlet and outlet, were placed 150 g (0.037 mol, 50% solids) of the monomer solution of Ex. 2, followed by 100 g isobutylmethylketone and 0.75 g n-octylmercaptan (1% on solids). After purging the reactor with nitrogen, the temperature of the reaction mixture was raised to about 65°C and 0.75 g (0.5% on solids weight) of 2,2'-azobisisobutyronitrile (AIBN) was added. The reaction mixture was refluxed at about 65°C for 16 hours. The reaction was substantially complete as indicated by gaschromatography. After cooling a yellow solution of homopolymer according to the invention was obtained. The solution contained 30% polymer solids.

Example 11

Into a reactor flask as described in Example 10 are added 105 g of the monomer solution, Ex. 2, 22.5 g ethylacrylate and 122.5 g isobutylmethylketone and 0.75 g n-octylmercaptan. After purging the reactor with nitrogen, the temperature of the reaction mixture was

- 21 -

raised to 65°C and 0.75 g AIBN was added. The polymerization was complete after 16 hours. The resulting yellow solution was filtered and contained 30% solids.

5

Example 12 - 25

In these examples, homopolymers and copolymers according to this invention, specified in Table 3, were prepared and diluted to 0.5% solids in 10 isobutylmethylketone or isopropanol (see Table 3). These dilutions were sprayed using "hand spray" equipment onto textile substrates (0.5% solids on fabric (SOF)) and grain leather (0.018 g/m², 0.2 g/sqft) and were left to dry for 24 hours at ambient 15 temperature before the following tests were carried out: oil repellency (OR), water repellency (WR) and resistance to waterspray (SR).

The test results are set forth in Table 3.

20. TABLE 3

Ex No.	No. SR	Fluoro- monomer		<u>Solvent</u>	PES/ Cotton			Leather grain		
		Table 1	Como- nomer		OR	WR	SR	OR	WR	
25	10	2		IPA	2	3	70	7	7	90
	11	2	EA	IPA	3+	4	80	4	6	80
	12	3		MIBK	3	5	70	2	4	70
	13	3	isoBMA	IPA	6	6	75	5	7	90
30	14	4		MIBK	4	4	80	6	2	75
	15	4	LA	MIBK	4	4	80	3	8	75
	16	5		MIBK	5	6	80	7	3	85
	17	5	BenzMa	MIBK	4	6	75	2	5	90
	18	6		MIBK	3	7	75	5	4	75
35	19	6	glycidlMA	MIBK	1	3	70	3	4	70
	20	7		MIBK	5	5	75	7	5	90
	21	7	AAEMA	MIBK	4	4	70	2	3	80
	22	8		IPA	2	3	70	3	2	75
	23	8	tBA	IPA	4	8	80	3	6	80
40	24	9		MIBK	4	3	70	6	7	75
	25	9	tBAEMA	IPA	4	5	85	5	9	70

- 22 -

Chemical structure of the comonomers of table 3

EA	Ethylacrylate	$\text{CH}_2=\text{CH}-\text{C}(\text{O})\text{OC}_2\text{H}_5$
isoBMA	Isobutylmethacrylate	
5		$\text{CH}_2=\text{C}(\text{CH}_3)-\text{C}(\text{O})\text{OCH}_2\text{CH}(\text{CH}_3)_2$
LA	Laurylacrylate	$\text{CH}_2=\text{CH}-\text{C}(\text{O})\text{OC}_{12}\text{H}_{25}$
BenzMA	Benzylmethacrylate	 - $\text{CH}_2\text{OC}(\text{O})-\text{C}(\text{CH}_3)=\text{CH}_2$
glycidylMA	Glycidylmethacrylate	$\text{CH}_2=\text{C}(\text{CH}_3)-\text{C}(\text{O})\text{OCH}_2\text{CH}(\text{CH}_2\text{O})$
10	AAEMA	AcetoacetoxyethylMA $\text{CH}_2=\text{C}(\text{CH}_3)\text{C}(\text{O})\text{OCH}_2\text{CH}_2\text{OC}(\text{O})\text{CH}_2\text{C}(\text{O})\text{CH}_3$
tBA	t-butylacrylate	$\text{CH}_2=\text{CH}-\text{C}(\text{O})\text{OC}(\text{CH}_3)_3$
tBAEMA	t-butylaminoethylMA	$\text{CH}_2=\text{CH}-\text{C}(\text{O})\text{OCH}_2\text{CH}_2\text{NHC}(\text{CH}_3)_3$
15		

Solvents of table 3

IPA = Isopropylalcohol
MIBK = Methylisobutylketone

20 Example 26

Following the same method used in Example 10, a copolymer was prepared using as monomers 75 g (50% solids solution) fluorochemical monomer Ex. No. 4 and 18.7 g t-butylaminoethylmethacrylate,

25



followed by 137.5 g isobutylmethylketone and 0.75 g n-octylmercaptan. After purging the reactor with nitrogen, the temperature of the reaction mixture was raised to 65°C and 0.75 g AIBN was added. After 16 hours, the mixture was permitted to cool and gas chromatography indicated complete conversion. The resulting solution contained about 30% solids.

- 23 -

This solution was diluted and applied as described in Examples 12 - 25 and the following results were obtained:

	Polyester/cotton	OR = 2	WR = 4	SR = 70
5	grain leather	OR = 3	WR = 8	SR = 75

Examples 27 - 30

In Examples 27, 28, 29 and 30, five different substrates other than textile and leather were treated 10 with polymers corresponding to No. 10, 13, 20 of Table 3 as indicated in Table 4. These polymer solutions, Nos. 10, 13, 20, were diluted to 3.4% solids, in the same solvent as mentioned in Table 3, and each time 3 g of the diluted solution was sprayed onto the different 15 surfaces of about 160 cm².

The substrates were left to dry at room temperature for 24 hours, and evaluated together with an untreated substrate, Example 30, for oil repellency (OR), water repellency (WR) and spray rating (SR).

20

TABLE 4

Ex No.	Polymer <u>Table 3</u>	Stone			Wood			Plastic			Glass			Metal			
		OR	WR	SR	OR	WR	SR	OR	WR	SR	OR	WR	SR	OR	WR	SR	
25	27	10	4	7	80	6	8	85	8	10	90	8	10	90	8	10	85
	28	20	4	7	85	6	7	90	8	10	90	8	10	90	8	10	90
	29	13	5	5	75	8	7	80	8	10	90	8	10	85	8	10	85
	30	-	0	0	0	0	1	50	0	0	75	0	0	80	0	0	80

- 30 * WOOD : Multiplex
 * STONE : Red Brickstone
 * PLASTIC : Polyesterfolie
 * METAL : Inoxplate

35

Examples 31 - 42

In Examples 31 to 42, (0.018 g/m², 0.2 g/sqft) of 1.5% solids solution of polymer no. 13 of the 40 invention and solutions of prior art fluorochemical compositions were sprayed onto chromium tanned grain and suede cow leather from Union Gantoise. The test results

- 24 -

are shown in table 5, the samples were tested for OR, WR, SR and the bally water transfer test (See Scotchgard Leather Protector Manual, published by 3M Protective Chemical Products Division, January 1990).

5 In Examples 33 - 40, fluoroochemical compositions which contain environmentally unacceptable solvents were used. In Examples 41 and 42, compositions were tested which use isopropanol as solvent. In Examples 31 and 32, the compositions according to the invention 10 were tested.

As can be seen from Table 5, the compositions according to the invention show a similar performance compared to the Examples 33 - 40 which use 15 environmentally unacceptable solvents. In comparison to compositions tested in Examples 41 and 42 which also use isopropanol as solvent, the performance of the 20 compositions according to the invention is much better.

20 TABLE 5

	Ex.	Product	Solids In	Diluted	Leather type	BALLY TEST				
						OR	WR	Sr	time	ab-sorp-tion
25	31	no.13	30%	IPA	U.G. grain	5	4	100	15'	16%
	32				U.G. suede	6	6	100	15'30"	16%
30	33	A	3%	IPA/BuAc	U.G. grain	3	7	90	12'	13%
	34				U.G. suede	5	6	80	12'	20%
	35	B	25%	Hept./BuAc	U.G. grain	5	7	100	9'34"	26%
	36				U.G. suede	5	9	100	8'49"	29%
35	37	C	40%	BuAc	U.G. grain	1	1	50	9'48"	14%
	38				U.G. suede	1	1	70	11'45"	28%
	39	EP-A2-0100277	40%	BuAc	U.G. grain	6	7	80+	9'	11%
	40				U.G. suede	6	9	100	10'10"	7%
40	41	U.S. 4,778,915	31%	IPA	U.G. grain	1	3	80	5'	9%
	42				U.G. suede	2	3	80	7'	19%

45 A = A fluoroochemical urethane prepared according to U.S. Patent No. 3,398,182 using fluorocarbon compound V, hydrocarbon compound LI and reactive compound J.

- 25 -

- B = A fluorochemical copolymer prepared according to U.S. Patent No. 3,341,497 using 65% N-methyl per-fluorooctanesulfonamidoethyl methacrylate and 35% octadecyl methacrylate.
- 5 C = A fluorochemical urethane prepared according to U.S. Patent No. 3,398,182 using fluorocarbon compound V, 2-ethyl hexanol as the hydrocarbon compound and reactive compound J.
- 10

Examples 43-43

- In Example 43, the organic polymer solution of
- 15 Example 13 was converted to an aqueous dispersion by adding 200 g of the organic solution to an aqueous phase (222 g water) which contained anionic surfactant (14.4 g SERMUL EA 146) and 18 g ethylene glycol under ultra turax treatment at 65°C. This was followed by two passes
- 20 through a high shear homogenizer. The resulting dispersion was stripped of the isobutylmethylketone at reduced pressure with a water aspirator and a pot. temperature of 65°C to yield an anionic emulsion with 22% total solids.
- 25 In Example 44, the procedure described in Example 43 was used to prepare a cationic emulsion except 200 g of the polymer solution of Example 13 was substituted for the polymer of Example 13, and instead of the anionic surfactant SERMUL EA 146, cationic surfactant
- 30 ETHOQUAD HT/25 (4.8 g) was used.

- In Examples 43 and 44, two different rainwear fabrics were treated with the cationic and anionic aqueous emulsions of fluorochemical polymer of composition nos. 13 and 23 of Table 3, as indicated in
- 35 Table 6. The fabrics were treated in a padding operation, dried at 150°C for 5 min., and evaluated together with untreated fabrics, Example 45, for initial oil repellency (OR), water repellency (WR) and resistance to a waterspray (SR). An OR value of 3, and a SR of 70 or
- 40 greater is particularly desirable for this application.

- 26 -

TABLE 6

Ex. Table 3 no.	Surfactant 8% on solids	% SOF	PES/COTTON			Nylon PA 66			
			OR	WR	SR	OR	WR	SR	
43	13	Sermul EA146	0.3	2	4	75	3	2	70
5	44	Ethoq. HT/25	0.3	3+	3	75	3+	3	70
	45	/	/	/	0	0	0	0	0

Examples 46 - 47

In Example 46, the anionic aqueous emulsion of composition no. 23 was evaluated for drum treatment on a chrome tanned full grain cow hide. The purpose of a drum treatment is to incorporate the fluoroochemical into the protein structure of the leather. Example 47 was untreated.

15

TABLE 7

Ex. Polymer	Bally Test						
	Water- transfer			Absorp- tion % After 2 hrs.			
	OR	WR	SR	OR	WR	time	
46 23	2	3	70	1	3	>120	75.51
47 untreated	0	0	0	0	0	0	0

25

30

35

- 27 -

CLAIMS:

1. Polymers or copolymers comprising the polymerization product of

- 5 a) diisocyanates with a perfluoro compound or an epichlorhydrin adduct thereof, said perfluoro compound having a terminal hydroxyl, thiol, primary or secondary amino group, attached to the perfluoroalkyl group directly via an alkylene bridge or indirectly via an alkylene bridge and a sulphonamido, carbonamide, ether, thioether, sulphonyl or carboxylic ester group between the perfluoroalkyl and the alkylene group, and
- 10 b) (meth)acrylic esters of a three hydroxyl groups containing compound.

2. Polymers or copolymers according to claim 1, wherein the (meth)acrylic esters are the reaction products of an equimolar reaction between (meth)acrylic acid and a three hydroxyl group containing compound.

3. Polymers or copolymers according to claim 1 wherein the diisocyanates used are aliphatic, alicyclic or aromatic.

4. Polymers or copolymers according to claim 1 wherein the comonomers for preparing the copolymer include moieties derived from vinyl ethers, vinyl esters 30 allyl esters, vinyl ketones, styrene, vinylamide, acrylamides, maleates, fumarates, acrylates and methacrylates.

5. Polymers or copolymers according to claim 1 35 wherein acrylates and methacrylates are used as comonomers.

- 28 -

6. Polymers or copolymers according to claim 1
wherein the fluoro compounds are perfluoro alkyl
substituted compounds with a terminal hydroxyl group.

5 7. Polymers or copolymers according to claim 6
wherein the perfluoro alkyl substituted compounds are
N-alkyl(perfluorooctane)sulphonamido alkyl alcohols or
telomer alcohols.

10 8. Polymers or copolymers according to claim 1
wherein the three hydroxyl groups-containing compound is
a alkanetriol or a nitrilotrialkanol.

9. Fluoroacrylate monomer obtainable by the
15 reaction of

- a) diisocyanates with a perfluoro compound or an
epichlorhydrinadduct thereof, said perfluoro
compound having a terminal hydroxyl, thiol,
primary or secondary amino group, attached to
the perfluoroalkyl group directly via an
alkylene bridge or indirectly via an alkylene
bridge and a sulphonamido, carbonamide, ether,
thioether, sulphonyl or carboxylic ester group
between the perfluoroalkyl and the alkylene
group, and
- b) (meth)acrylic esters of a three hydroxyl
group-containing compound.

10. Fluoroacrylate monomer of claim 9 wherein the
30 (meth)acrylic esters are the reaction products of an
equimolar reaction between (meth)acrylic acid and a three
hydroxyl group containing compound.

11. Fluoroacrylate monomer according to claim 9
35 wherein said diisocyanates are aliphatic, alicyclic or
aromatic.

- 29 -

12. Fluoroacrylate monomer according to claim 9
wherein the three hydroxyl groups containing compound is
a alkanetriol or a nitrilotrialkanol.

5 13. Fluoroacrylate monomer according to claim 9
wherein the fluoro compounds are perfluoro alkyl
substituted compounds with a terminal hydroxyl group.

14. Fluoroacrylate monomers according to claim 9
10 wherein the perfluoro compounds are N-alkyl-
(perfluorooctane)sulphoneamido alkyl alcohols or
telomeralcohols.

15. A process for preparing the polymers or
15 copolymers of claim 1 comprising the steps of
a) forming a fluoroacrylate monomer prepared by
reacting
a₁) a diisocyanate with a perfluoro compound
or an epichlorhydrinadduct thereof, said
perfluoro compound having a terminal
hydroxyl, thiol, primary or secondary
amino group, attached to the perfluoro-
alkyl group directly via an alkylene
bridge or indirectly via an alkylene
bridge and a sulphonamido, carbonamide,
ether, thioether, sulphonyl or carboxylic
ester group between the perfluoroalkyl and
the alkylene group, and
a₂) (meth)acrylic esters of a three hydroxyl
groups containing compound
and
b) polymerizing the monomer by homopolymerization
or copolymerization in an organic solvent or
in an aqueous emulsion.

- 30 -

16. Process according to claim 15, wherein the (meth)acrylic esters are the reaction products of an equimolar reaction between (meth)acrylic acid and a three hydroxyl group containing compound.

5

17. Process according to claim 15 wherein the temperature range for the polymerization reaction is from 50 to 110°C.

10 18. Process according to claim 15 wherein the total monomer concentration is from 5 to 60% by weight.

19. Process according to claim 15 wherein the reaction is conducted in the presence of a catalyst.

15

20. Treatment agent comprising the polymers or copolymers of claim 1 and a environmentally acceptable solvent.

20 21. Treatment agent according to claim 20, wherein the solvent is an alkanol, water, a ketone, ester or a mixture thereof.

22. Treatment agent according to claim 20 wherein
25 the solvent is water or isopropanol or a mixture thereof.

23. Treated substrates having oil and water repellency comprising substrates selected from the group consisting of textiles, papers, non-woven articles,
30 leather, plastic, wood, metal, glass, stone and cement having applied thereto the polymers and copolymers of claim 1.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 92/03300

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)⁶

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 C08G18/28; C08G18/67; D06M15/576

II. FIELDS SEARCHED

Minimum Documentation Searched⁷

Classification System	Classification Symbols
Int.Cl. 5	C08G ; D06M

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched⁸III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹

Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
A	EP,A,0 414 155 (ASAHI GLASS) 27 February 1991 see page 4, line 56 - page 8, line 27; claims 1-3 ---	1
A	GB,A,1 011 976 (3M) 1 December 1965 see page 1, line 40 - page 5, line 5; claims 1,2,5 ---	1
A	US,A,2 803 615 (AHLBRECHT ET AL) 20 August 1957 cited in the application ----	1

¹⁰ Special categories of cited documents :¹⁰

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

- "Z" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search

12 AUGUST 1992

Date of Mailing of this International Search Report

21.08.92

International Searching Authority

EUROPEAN PATENT OFFICE

Signature of Authorized Officer

BOURGONJE A.F.

ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO. US 9203300
SA 60521

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information. 12/08/92

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP-A-0414155	27-02-91	JP-A- US-A-	3076873 5100954	02-04-91 31-03-92
GB-A-1011976		CH-A- DE-A- FR-A- NL-C- NL-A- US-A-	430921 1520251 1336689 130119 278275 3255131	29-01-70
US-A-2803615		CH-A- DE-B- DE-B- FR-A- GB-A-	357872 1106960 1220383 1172081 857689	